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54 Apparatus for determining the concentration of a liquid mixture

57 The apparatus has a measuring crystal (MQ) which can be wetted by the liquid mixture and which is energized to induce thickness-shear vibrations, and whose resonance frequency changes as a function of the concentration, and also has a reference crystal (RQ) situated in a reference liquid. An evaluation circuit for the output signals from the quartz resonators sends an output signal corresponding to the concentration. The apparatus (1) comprises a measuring head (2) having a measuring chamber (5) which is open to the liquid mixture, and a directly adjacent, closed reference chamber (6) which contains the reference liquid and in which the measuring crystal (MQ) and the reference crystal (RQ), respectively, are contiguously placed. The measuring crystal and reference crystal are each the frequency-determining element in a respective self-energized resonance circuit (Figure 5) which is designed so that the crystal in each case vibrates just below its series resonance frequency.

[See source for figure]

[See Figure 1 for key]

The following information is taken from documents submitted by the applicant.

Description

The invention relates to an apparatus for determining the concentration of a liquid mixture according to the preamble of Claim 1. Such an apparatus may be used, for example, to determine the concentration of a water/antifreeze mixture, such as in a heating unit or in the cooling circuit of an engine.

Such an apparatus having a measuring quartz crystal and a reference quartz crystal is known from US 4,741,200. The measuring crystal and reference crystal are placed in the parallel legs of a bridge circuit and together are energized by an oscillator to induce thickness-shear vibrations. The measuring crystal is submerged in the liquid to be measured, whereas the reference crystal is placed in air or a reference liquid, for example. A resistor is situated in the first parallel leg of the bridge containing the measuring crystal, and a balancing resistor is situated in the second parallel leg containing the reference crystal. The bridge signal is received between each crystal and its associated resistor and is transmitted to the inputs of an amplifier, where the offset voltage is measured. The concentration of the liquid mixture is then directly displayed in a subsequent detector having a display.

For determining the concentration, in this case use is made of the fact that the viscosity of the liquid mixture significantly changes as a function of the concentration, and that the frequencies of the shear vibrations from the measuring crystal and reference crystal likewise are strongly dependent on the viscosity.

Before a measurement, the bridge is balanced and calibrated by placing both crystals in air or a reference liquid and adjusting the oscillator frequency to a value approximately 0.2 percent above the resonance frequency. The balancing resistance is then changed until a minimum offset voltage is achieved. For the measurement the reference crystal remains in air or the reference liquid, and the oscillator frequency is varied over a specified frequency range. The offset voltage shows two peaks, one of the peaks corresponding to the resonance of the reference crystal and the other peak corresponding to the resonance of the measuring crystal in the liquid mixture to be measured. By use of these two values together with a calibration curve, the viscosity of the liquid mixture and thus the concentration of the liquid in the mixture to be measured may be determined.

As described in this U.S. patent, the frequency of the oscillator must be very stable to allow the resonance and antiresonance of the crystals to be determined. The frequency must be stable between approximately 1 to 10 Hz to obtain results of sufficient accuracy.

Furthermore, the method is relatively complicated, since a broad frequency range must be continuously traversed by the oscillator, and manipulation of the two crystals in the bridge circuit is quite involved. In addition, there are no provisions in this apparatus for taking into account the dependence of viscosity on pressure and temperature, resulting in faulty measurements of the concentration.

S. Bruckenstein and M. Shay have proposed an apparatus referred to as a quartz crystal microbalance in Electrochimica Acta, Vol. 30, No. 10, 1985, pages 1295-1300, having a measuring crystal and a reference crystal placed in air, the two crystals being connected to an intrinsic oscillator circuit. The output signals from the reference crystal are used as clock signals to determine the difference in frequencies in the two crystals, which is a measure of the viscosity of the liquid mixture and thus of the concentration of the liquid in the mixture to be measured. An electrochemical cell is provided for this apparatus into which the liquid mixture, in particular an electrolyte, is filled. The reference crystal is located relatively far from the position of the measuring crystal. The entire apparatus is not designed for taking into account pressure and temperature effects on the liquid mixture.

The object of the invention is to specify an apparatus for measuring the viscosity of a liquid, which has a simple design and provides accurate measurements, whereby pressure and temperature effects are substantially corrected as well, and which can be used for various applications.

This object is achieved according to the invention by the features stated in the characterizing portion of Claim 1.

Accordingly, the apparatus has a measuring head in which the measuring crystal and reference crystal are placed directly adjacent to one another, i.e., separated only by a spacer element. A compact sensor is thus obtained in which the two crystals are exposed to essentially the same environmental conditions, so that the pressure and temperature, for example, for the measuring

crystal and reference crystal are generally approximately equal, and the effects thereof on the measurement results may be easily compensated for, for example by using appropriate calibration curves. Each of the crystals is the frequency-determining element in a respective self-energized resonance circuit which is designed so that each crystal vibrates just below (several kiloherz, for example) the series resonance.

The measuring chamber and the reference chamber are located directly adjacent to one another, whereby the base of each chamber or at least a portion thereof is formed in each case by a small quartz plate. The bases of the two chambers are contiguously situated and are optionally separated by a spacer element or, for example, a shield, to avoid mutual mechanical and electrical influences. Of course, it is also possible to provide the measuring crystal and reference crystal on a common quartz substrate, so that the measuring chamber and reference chamber are directly laterally adjacent to one another.

The apparatus according to the invention may be designed very compactly and used for various applications. It is possible, for example, to install the measuring crystal and reference crystal in a compact measuring head, and to connect same to a handle in which the evaluation circuit and a display are located. A portable sensor is thus provided by which the concentration of a liquid mixture may be quickly determined. It is also possible to permanently install the measuring head in the reference circuit of a heating unit, for example, and to install the evaluation circuit in a switch box. This sensor is then used to indicate the concentration of the antifreeze and to give a warning before the antifreeze is depleted. To this end, the measuring head is preferably positioned in a cell, one wall of which is provided with a filter which keeps particles present in the circuit from reaching the measuring head. Otherwise, the cell is liquid-tight.

The evaluation circuit may be designed very simply: the circuit has a mixer which combines the output signals from both oscillators, the output signal from the mixer being connected to a comparator circuit and display circuit in which the difference between the frequencies of the measuring crystal and the reference crystal is determined and converted into numerical values for the viscosity. Preferably a frequency/voltage transformer is also provided between the mixer, to which analog frequencies are sent, so that the evaluation circuit evaluates a predetermined voltage.

Further embodiments of the invention result from the subclaims.

The invention is explained in greater detail in embodiments, with reference to the drawings:

Figure 1 shows a block diagram of an apparatus according to the invention for determining the concentration of a liquid mixture;

Figure 2 shows a schematic, partial sectional view of a hand implement for measuring the concentration, using a measuring head designed according to the invention;

Figure 3 shows an exploded view of the measuring head from Figure 2;

Figure 4 shows the configuration of a measuring head in a cell for permanently mounting the sensor in a liquid circuit;

Figure 5 shows a self-energized resonance circuit together with the frequency-determining measuring crystal or reference crystal for a measuring head according to the invention;

Figure 6 shows the calculated negative change in the resonance frequency of a quartz crystal as a function of the concentration of a cooling liquid composed of water and antifreeze for 20°C and 80°C, with a reference liquid composed of water and 30 vol-% antifreeze;

Figure 7 shows a measurement diagram for various concentrations of antifreeze in a cooling liquid for temperatures between 40°C and 80°C, with a reference liquid composed of water and 30 vol-% antifreeze, plotted as a function of the output voltage of an evaluation circuit; and

Figure 8 shows the phase response of the admittances of the measuring crystal and reference crystal, whereby phase responses for various fluids and concentrations are illustrated for the measuring crystal.

The embodiments are explained in conjunction with the determination of the concentration of antifreeze in cooling water, for example in a heating or cooling unit or in the cooling circuit of the engine in a motor vehicle. The addition of antifreeze to the cooling water prevents both

freezing and boiling over. Such an addition also provides protection from rust and corrosion without damaging rubber hoses. Modern antifreeze agents are intended to be contained in an optimum concentration in the cooling water, between 40% and 60%, for example, over the entire year. The addition of antifreeze raises the boiling point of the cooling liquid and lowers its freezing point. The viscosity of the cooling liquid is greatly dependent on the concentration of the antifreeze. If glycol is used as antifreeze agent, at 30°C the viscosity increases from approximately 1 cP at 0 vol-% glycol in water to approximately 10 cP at 75 vol-%. This change in viscosity can be determined by use of a sensor 1, the design of which is schematically illustrated in Figure 1.

The sensor has a measuring head 2 in which two quartz resonators, namely a measuring crystal MQ and a reference crystal RQ, are situated. The electrical circuitry for the two crystals is dimensioned in such a way that the crystals vibrate just below their respective series resonance frequencies. The resonance frequencies of the two crystals are designed to be different. In practice, the resonance frequencies are several megahertz, the resonance frequency of the reference crystal RQ being selected to be several kilohertz, for example approximately 20 kilohertz, higher than that of the measuring crystal. This can be achieved, for example, by making the surface of the measuring crystal plate thicker by sputtering with gold for some time. An oscillator O1 with the frequency F1 and an oscillator O2 with the frequency F2 are connected to measuring crystal MQ and reference crystal RQ, respectively. The crystals and oscillators are inserted into a self-energized oscillator circuit which is described in greater detail in conjunction with Figure 5. The oscillator frequencies F1 and F2 are fed to a mixer M in which the difference in frequencies AF is determined. This difference in frequencies is converted in a frequency/voltage transformer W into a voltage which in an evaluation circuit A is converted to an associated concentration value which is outputted to a display on which the concentration of antifreeze in the cooling liquid appears, in volume percent, for example. A thermocouple T is also provided in the measuring head 2 whose output signal indicating the temperature of cooling and reference liquids is likewise fed to the evaluation circuit A, so that the concentration values can be corrected for temperature there.

Figure 2 illustrates a sensor 1, which can be used as a handheld tool, in a sectional view. Into the measuring head 2 is screwed a handle 3 which on its end has the evaluation circuit A with the

display D, an LED display, for example. The measuring head has a housing 4 with a cylindrical interior which is divided into a measuring chamber 5 and a reference chamber 6. On the outer end face of the housing the measuring chamber has a free opening 7, the base of which is formed by the measuring crystal MQ which is placed parallel to the end face and which is supported by a spacer ring 8 whose ring opening corresponds approximately to the diameter of the measuring chamber. Between a circumferential collar 9 at the edge of the free opening 7 and the measuring crystal MQ an O-ring 10 is placed which forms the side wall of the measuring chamber and seals off same in a liquid-tight manner from the rest of the interior of the measuring head. The reference crystal RQ is mounted on the side of the spacer ring 8 opposite from the measuring crystal and forms the base of the reference chamber 6. The side wall of the reference chamber is formed by a subsequent O-ring 11 and the inner wall of a stainless steel ring 12 whose ring opening corresponds approximately to the inner diameter of the spacer ring. The free opening of this stainless steel ring is covered by a diaphragm seal 14, for example a Viton gasket. The entire system is closed by a lid 15 and is clamped together by screws which are screwed into the housing 4. The lid 15 has a cavity 16, traversing the opening in the stainless steel ring 12, which communicates with the surroundings through an additional opening 17.

A reference liquid, for example a mixture of 70 vol-% water and 30 vol-% antifreeze, is filled into the reference chamber 6. As a result of the Viton gasket and the lid 15 it is possible for the volume of the reference chamber to change without significant variation of the pressure on the reference crystal RQ.

Connecting lines, not shown, are soldered to the crystals and are led to the evaluation circuit through the screw opening for the handle. The electrical contact between the crystal and connecting lines may also be achieved in another manner, such as by compression inside the system, etc.

After the apparatus is calibrated, for a measurement the measuring head 2 is submerged in the cooling liquid so that the cooling liquid reaches the surface of the measuring crystal through the free opening 7. The series resonance frequency of the measuring crystal is correspondingly set to a value that is dependent on the viscosity value of the cooling liquid, and is thus dependent on the concentration of the antifreeze. The expected change in the resonance frequency of the

measuring crystal as a function of the viscosity of the mixture is shown in Figure 6 for 200 [sic; 20°?] and 40°C [sic; 80°?], the reference liquid used being water with 30 vol-% antifreeze.

Figure 7 illustrates the voltage subsequent to the frequency/voltage transformer (3 Hz = 1 nV) at different antifreeze concentrations, for cooling liquid temperatures of 40°C and 80°C. It can be seen that the slope of the curve is sufficient to obtain very accurate measurement values.

Figure 4 shows a modified sensor 1' which is suitable for a fixed installation of the measuring head 2, for example in the cooling circuit of a heating or cooling unit. The measuring head 2 is screwed into the hollow interior 30 of a cell 31 which is designed to be liquid-tight at the side walls and base and which is closed off on its top side by a filter 32, for example a fine-mesh screen, which allows the liquid being measured, but not dirt particles, to pass through. In this manner contamination of the measuring head, and thus measurement errors, are prevented.

In Figure 5 the circuitry for one of the crystals, in this case the measuring crystal, is illustrated. The circuitry for the reference crystal has the same design. The measuring crystal MQ is connected via a coupling capacitor 41 to the positive input 42 of a broadband video amplifier 43, the connection terminals of which have supply voltages U1 of +5 volts and U2 of –5 volts. The operational amplifier 43 has a very high amplification factor of 400 and higher, for example. In addition, a matched resistor 45 is provided between the positive input 42 and the negative input 44. A resistor 47 leads from the positive output 46 of the broadband video amplifier 43 to the base of a decoupling transistor 48 at whose emitter the output signal O is received via a decoupling circuit 49. The inverted output signal at a negative output 50 of the amplifier 43 is fed back to the negative input 44 of the amplifier 43 through a feedback resistor 51. A parallel circuit from two diodes connected antiparallel to ground is connected to the resistor 51, thereby making it possible to limit the amplitude. An appropriately sized resistor may be provided instead of the diodes.

The described circuit is extremely insensitive to interferences, and provides highly reproducible measurement results. The working point of the resonance circuit can be changed by changing the matched resistance. Thus, for example, the series resonance lies approximately at the first zero crossing of the phase response of the admittance (see Figure 8). It can be seen from this figure that a clear zero crossing is present for the measuring crystal in air, and a zero crossing is barely

present for water, but is not present for cooling liquids containing 50% or 30% antifreeze. For a conventional feedback with a 0° or 360° phase, the resonance circuit would no longer vibrate there. However, by appropriate adjustment of the matched resistance a working point may be selected for a phase of 75°, in this case for example, whereby the circuit vibrates in spite of the damping caused by the viscosity of the cooling liquid.

In the above embodiments the measuring crystal and reference crystal were separate units. Of course, it is possible to attach the measuring electrode and reference electrode at different locations on a quartz resonator. It would also be possible to measure at the null phase with the resonance circuit.

Claims

1. Apparatus for determining the concentration of a mixture of at least two liquids, having a measuring crystal which can be wetted by the liquid mixture and which is energized to induce thickness-shear vibrations, and whose resonance frequency changes as a function of the concentration, and also having a reference crystal situated in a reference liquid, and having an evaluation circuit for the output signals from the quartz resonators which sends an output signal corresponding to the concentration, **characterized in that** the apparatus (1) comprises a measuring head (2) having a measuring chamber (5) which is open to the liquid mixture, and a directly adjacent, closed reference chamber (6) which contains the reference liquid and in which the measuring crystal (MQ) and the reference crystal (RQ), respectively, are contiguously placed, the measuring crystal and reference crystal each being the frequency-determining element in a respective self-energized resonance circuit (Figure 5) which is designed so that the crystal in each case vibrates just below its series resonance frequency.

2. Apparatus according to Claim 1, characterized in that the measuring crystal (MQ) and the reference crystal (RQ) respectively form at least a portion of a flat base of the measuring chamber (5) or reference chamber (6).

3. Apparatus according to Claim 2, characterized in that the bases of the chambers directly face one another.

4. Apparatus according to Claim 2, characterized in that the measuring crystal and reference crystal (MQ, RQ) are designed to be on a common small quartz plate.

5. Apparatus according to Claim 1, characterized in that the reference chamber (6) is designed so that a change in volume of the reference liquid is permitted.

6. Apparatus according to Claim 5, characterized in that the reference chamber has an elastic wall (14).

7. Apparatus according to one of the preceding claims, characterized in that the measuring crystal and reference crystal (MQ, RQ) are respectively connected to an oscillator (O1, O2), and the oscillators are connected to a mixer (M) for determining the difference in frequencies, and the output signal from the mixer is fed to an evaluation circuit (A).

8. Apparatus according to Claim 7, characterized in that a frequency/voltage transformer (W) is connected between the mixer (M) and the evaluation circuit (A).

9. Apparatus according to one of the preceding claims, characterized in that the series resonance frequencies of the measuring crystal (MQ) and the reference crystal (RQ) are in the megahertz range, and the series resonance frequency of the reference crystal (RQ) differs from that of the measuring crystal by a value in the kilohertz range.

10. Apparatus according to Claim 9, characterized in that the series resonance frequency of the reference crystal (RQ) is approximately 20 kilohertz higher than that of the measuring crystal (MQ).

11. Apparatus according to one of the preceding claims, characterized in that a temperature sensor (T) is provided in the measuring head (2) and is connected to a compensation circuit in the evaluation circuit (A) to compensate for temperature effects.

12. Apparatus according to one of the preceding claims, characterized in that the measuring head (2) has a housing (4) with openings located at two end faces (7, in 12) [sic], that each of the crystals (MQ, RQ) is placed inside the housing, separated by a spacer ring (8), and that the space between the free opening (7) in the front and the measuring crystal (MQ) is used as the measuring chamber (8), and the space between the reference crystal (RQ) and the opposite

closed opening in the housing is used as the reference chamber (7), the two chambers being sealed liquid-tight with respect to one another.

13. Apparatus according to Claim 12, characterized in that the opening in the reference chamber is closed off by a wall (14), in particular an elastic wall, which conforms to the changes in volume of the reference liquid contained in the reference chamber.

14. Apparatus according to Claim 13, characterized in that the wall (14) of the reference chamber (6) which conforms to the changes in volume is covered by a housing lid (15) having a cavity (16) which faces one of the reference chambers (6) and which has approximately the cross section of the opening (13) there, and which is connected to the outside surroundings through an opening (17).

15. Apparatus according to Claim 12, characterized in that a shaft (3) used as a holder for the measuring head can be inserted into the housing.

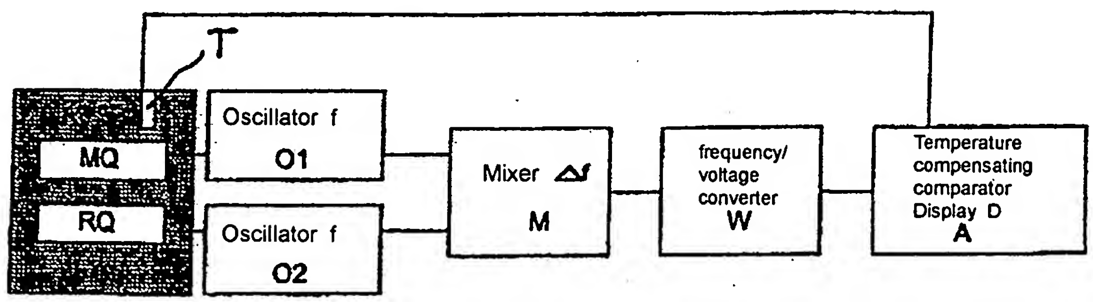
16. Apparatus according to Claim 15, characterized in that the shaft (3) is a handle in which the evaluation circuit (A) and a display (D) are housed.

17. Apparatus according to Claim 12, characterized in that the free opening (7) in the measuring chamber (5) is covered by a filter (32) which keeps particles present in the liquid to be measured from reaching the measuring crystal (MQ).

18. Apparatus according to one of the preceding claims, characterized in that the measuring head (2) is situated in a cell (31) and the evaluation circuit is situated outside the cell, and that a region of the otherwise liquid-tight cell is provided with a filter (32) which keeps particles present in the liquid to be measured from reaching the measuring head (2).

5 pages of drawings are attached.

Fig. 1 * 1


T
MQ
RQ
Oscillator f
O1
Oscillator f
O2
Mixer Δf
M
frequency/
voltage
converter
W
Temperature
compensating
comparator
Display D
A

1

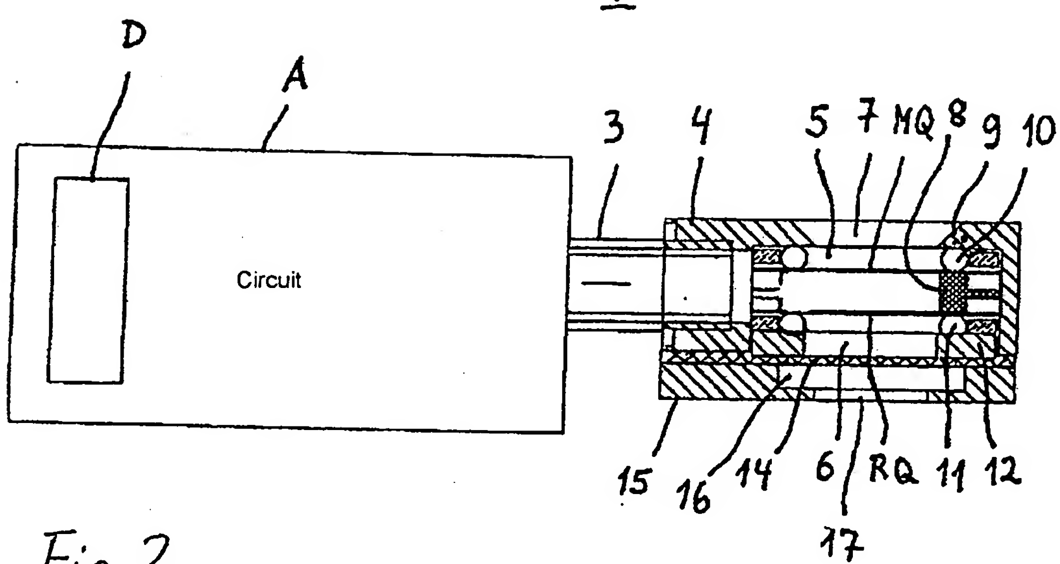

D
A
Circuit
3
4
5
7
MQ
8
9
10
15
16
14
6
RQ
11
12
17

Fig. 2

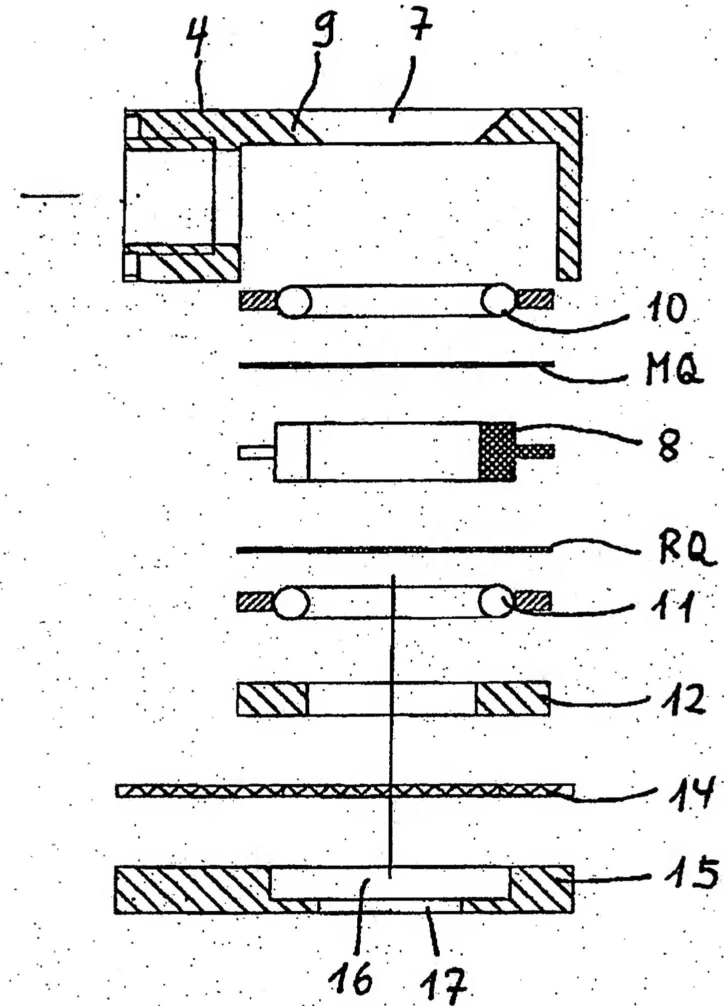


Fig. 3

DRAWINGS

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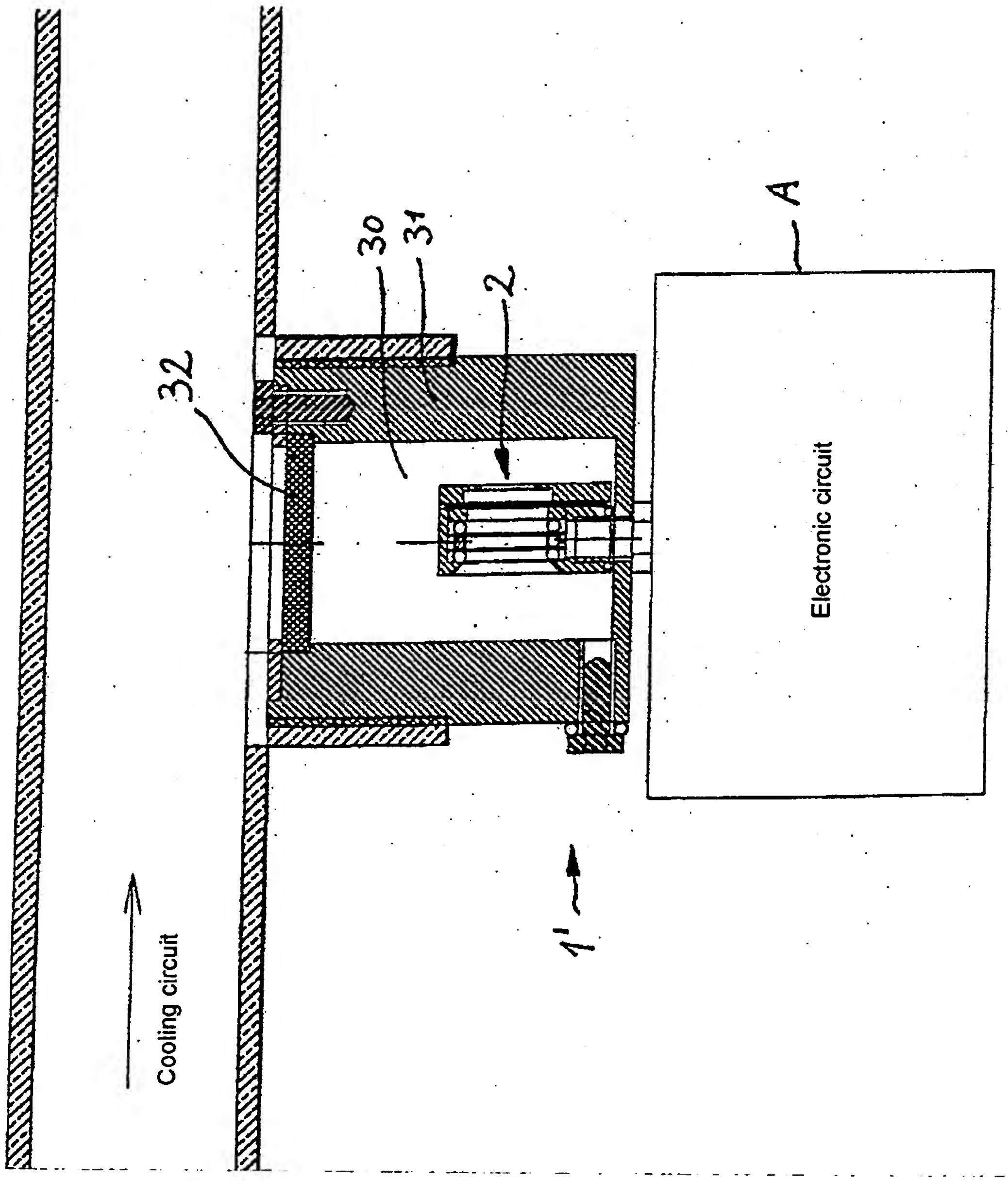
Date laid open for public inspection: January 18, 1996

Fig 4



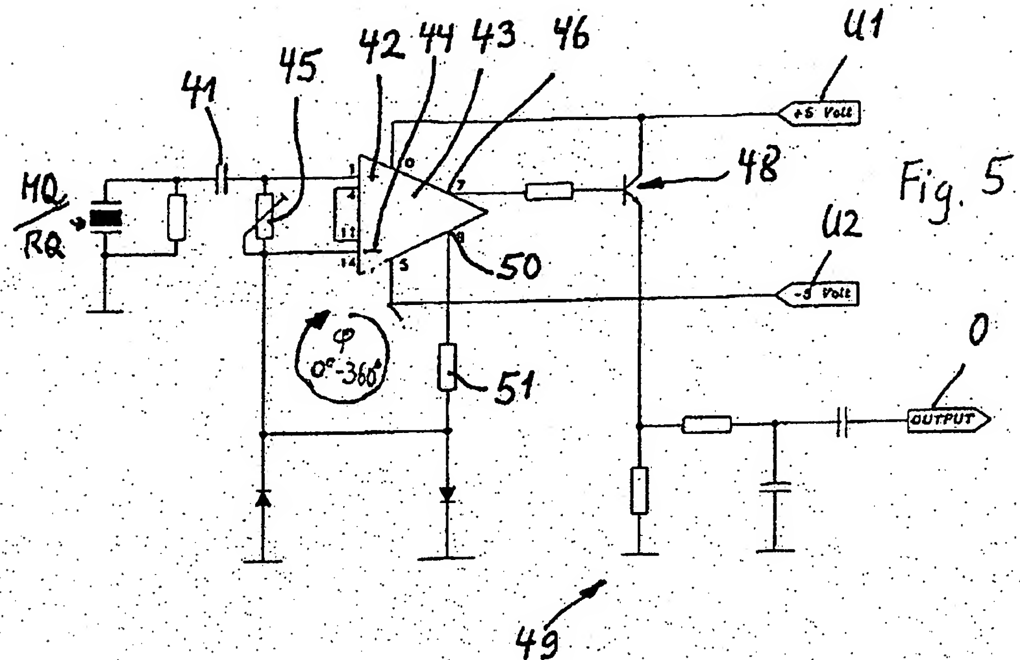
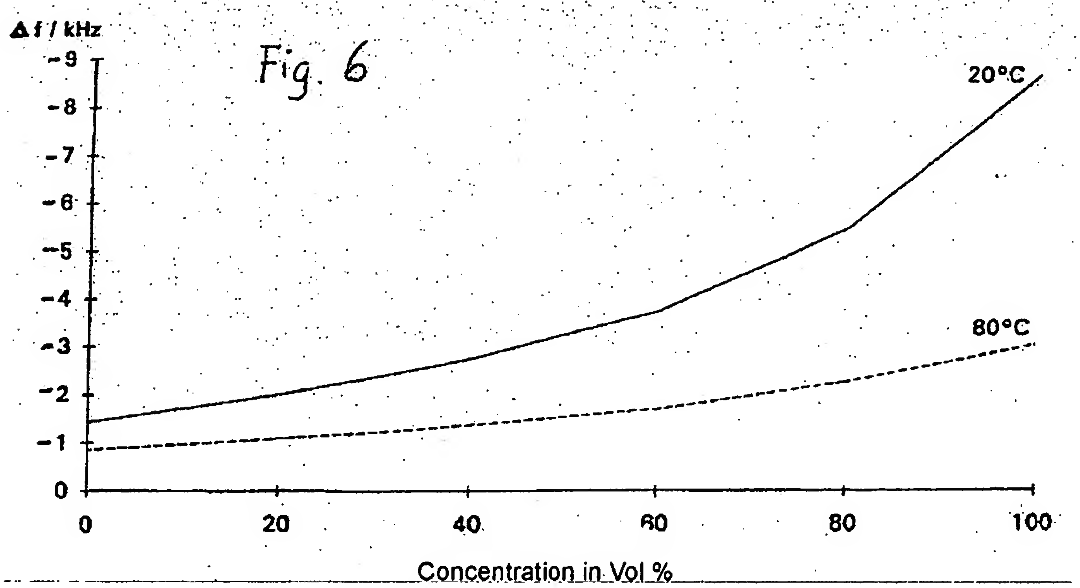

41
45
42
44
43
46
U1
+5 Volt
48
MQ
RQ
U2
-5 Volt
50
φ
0°-360°
51
0
OUTPUT
49

Fig. 5


Δf / kHz
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-8
-7
-6
-5
-4
-3
-2
-1
0
20°C
80°C
0
20
40
60
80
100
Concentration in Vol %

Fig. 6

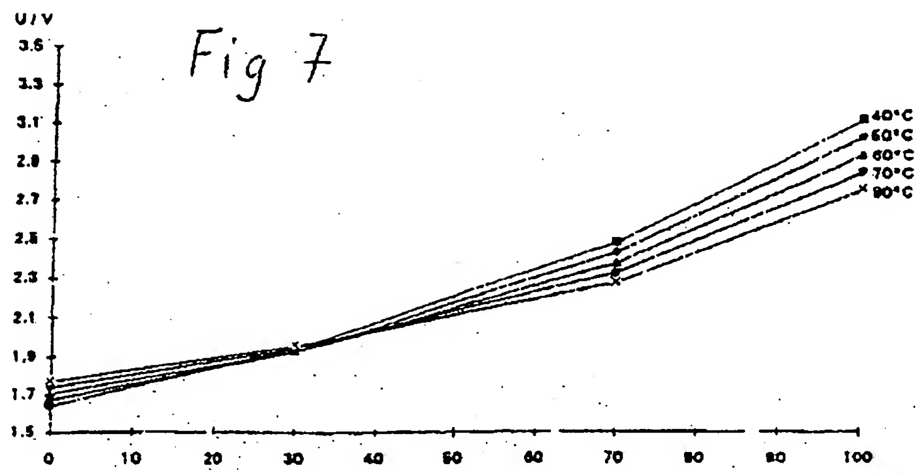

Fig 7

Phase of admittance

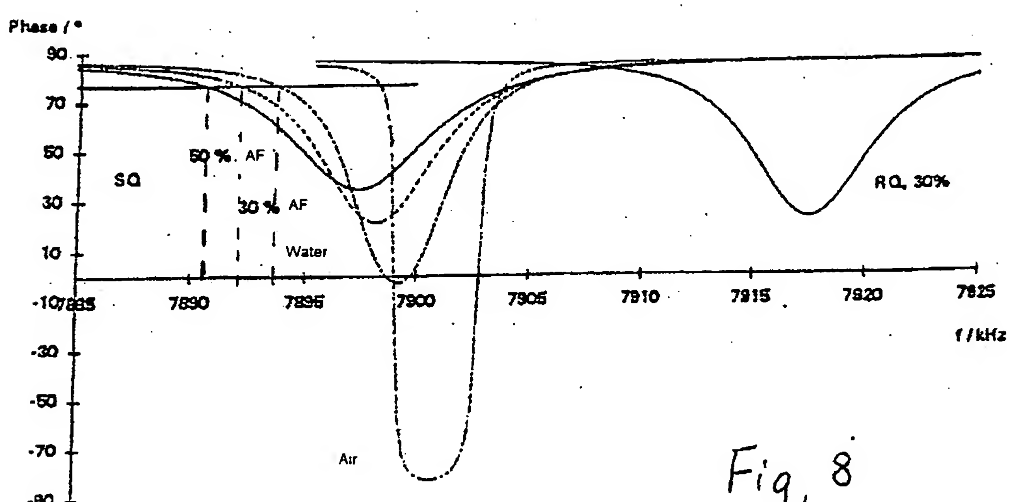

Fig. 8

Note: "AF" = Antifreeze